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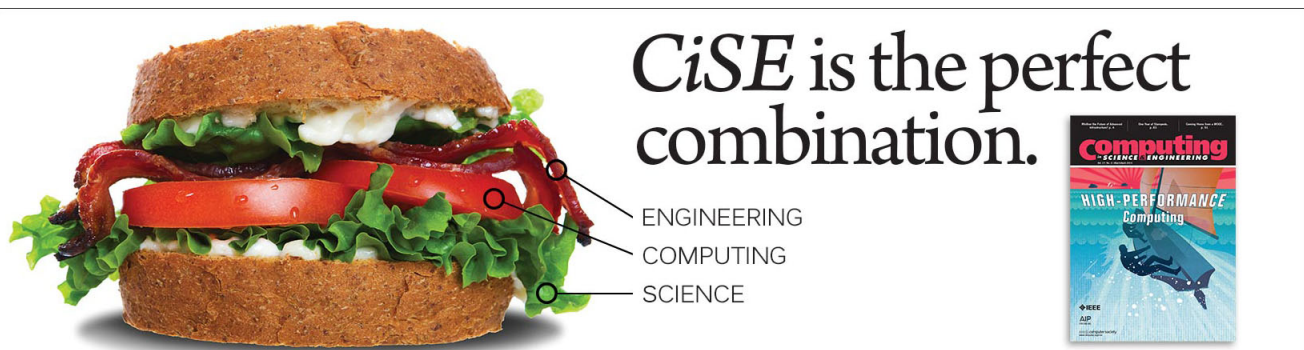
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Comparison of oxygen-chain models for late thermal double donors in silicon

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The electronic and atomic structures of the oxygen chains assigned to late thermal double donors (TDDs) in silicon are studied using accurate total-energy calculations. We find that the ring-type O-chain model is best suited for TDDs and better than the di-Y-lid-type O-chain model. The ring-type O chains have slightly alternating C_{2v} – C_{1h} symmetry consistent with the recent high-field electron paramagnetic resonance experiments. The spin densities of the double-donor states are located outside the region of the O atoms, which makes the hyperfine interaction of an unpaired donor electron with the ^{17}O nuclear spins very weak. © 2003 American Institute of Physics. [DOI: 10.1063/1.1563813]

Thermal double donors (TDDs) in silicon form a family of at least 17 closely related members (TDD0–TDD16),^{1–3} and appear consecutively under thermal heating of Czochralski-grown silicon at 350–550 °C.^{1,4} The TDDs are usually believed to consist of aggregated oxygen atoms. According to the interpretations of the electron paramagnetic resonance (EPR), electron–nuclear double resonance (ENDOR) and infrared (IR) absorption experiments, the TDDs have the following microscopic properties:

(i) *Atomic structure.* The TDDs have overall C_{2v} symmetry from TDD3 onwards, with the O atoms lying in the same (110) mirror plane and the C_2 symmetry axis pointing in the [001] direction.^{5–8} If the C_{2v} symmetry is to be strictly preserved during the growth of the TDDs, the O atoms should be added symmetrically in pairs.^{5–9} However, it is more natural to assume that the O atoms are added one by one in which case the C_{2v} and C_{1h} symmetries would occur alternately.^{5–7,9} There are indeed indications from high-field EPR experiments that some TDD members have lower C_{1h} symmetry, similar to what has been found for the closely related NL10 family.^{8,9} In addition, the C_2 symmetry axis does not contain any single O atom but contains a Si atom.^{6,7} Also, the IR absorption experiments indicate that the TDD structures become increasingly anisotropic for successively higher TDD numbers.¹⁰

(ii) *Electronic structure.* The spin densities of the double-donor states of TDD⁺s should become increasingly delocalized for higher order members.^{6,7} Similarly, the increase of the experimental IR $2p_{\pm}$ splittings indicates that the donor wavefunctions of TDDs become increasingly anisotropic for successively higher TDD numbers.¹⁰ In addition, it seems that the double-donor wavefunction has less extent along the [001] axis (C_2 symmetry axis) than the other directions.¹⁰

In the “di-Y-lid” model for TDDs the di-Y-lid core (O_{2Y}) consists of two O atoms (O_Y), each bonded to three near-Si atoms in a Y-shaped fashion.^{11,12} The corresponding O_{ki} – O_{2Y} – O_{li} chains ($k, l \geq 1$) with an even number of O

atoms (O_i denotes an interstitial O atom, $k = l$, the total number of O atoms $N = 2k + 2$) fulfill all the symmetry properties listed earlier; for an odd number of O atoms ($k \neq l$, $N = k + l + 2$), symmetry is lowered to C_{1h} .

On the basis of accurate total-energy calculations, we have recently put forward another O-chain model consisting of adjacent four-member rings (R) and flanking O_i .^{13,14} The R unit consists of two threefold coordinated O atoms (O_r) bonded to two common Si atoms.¹⁵ (One may also consider the O chain to consist of alternating Y and up-side-down Y units.) The O chains obtained for TDD0, TDD1, and TDD n ($1 < n < 8$) are O_i – O_{2r} ($N = 3$), O_{2i} – O_{2r} ($N = 4$), and O_i – O_{nr} – O_i ($1 < n < 8$, $N = n + 2$), respectively.^{13,14} (n is used to label the TDDs, and in the context of R-type chains n gives also the number of O_r). This same R-type O-chain model was also adopted in the recent study by Coutinho *et al.*¹⁶ (called O–2NN there). However, their TDD assignments differ from ours, which is discussed in more detail in Ref. 17.

We found from an earlier study up to $N = 10$, that the O_{4i} – O_{2Y} – O_{4i} chain ($N = 10$) possibly has a lower formation energy than the O_i – O_{8r} – O_i chain ($N = 10$).¹³ This indicates that some or all later TDDs ($n \geq 8$) may have the di-Y-lid chain structure. The aim of this letter is to compare calculated formation energies as well as electronic and atomic structures for O chains assigned to later TDDs ($N \geq 10$). The computational methods used are presented in Ref. 17. In particular, the longest elongated 162-atom-site supercell is used.

We have found that all structures containing Si interstitials or vacancies have significantly higher formation energies than oxygen-only structures, and that among the oxygen-only structures, the electrically active R- and di-Y-lid-type O chains as well as the electrically inactive staggered O chains have the lowest formation energies. These energies are shown for the neutral and doubly positively charged O chains in Figs. 1(a) and 1(b), respectively. Figures 1(a) and 1(b) correspond to extreme n - and p -type crystals, respectively. The O_{2Y} and O_i – O_{2Y} structures are unstable. The smallest stable di-Y-lid structures are O_i – O_{2Y} – O_i ($N = 4$, C_{2v}), O_i – O_{2Y} – O_{2i} ($N = 5$, C_{1h}), and O_{2i} – O_{2Y} – O_{2i} ($N = 6$, C_{2v}) that are all *deep donors*, as is obvious from the

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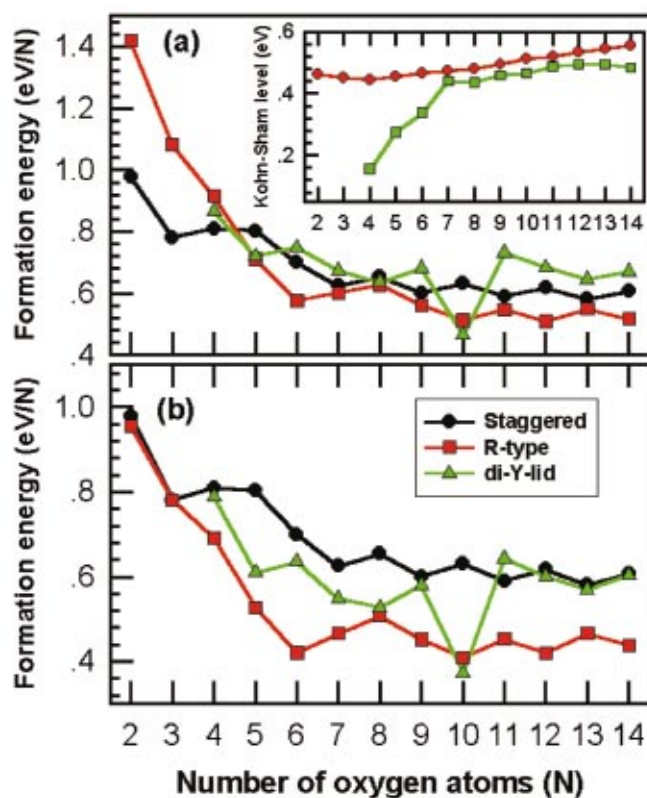


FIG. 1. (Color) (a) The calculated formation energies per oxygen atom of the neutral oxygen chains. N is the total number of oxygen atoms in the chain. At $N=4$, the R-type value is for $O_i-O_{2r}-O_i$ (TDD2). The inset shows the Kohn-Sham defect levels in the gap for the electrically active neutral chains. The corresponding Kohn-Sham levels of the staggered chains lie below the valence-band maximum. The valence-band maximum is at 0 eV. The calculated gap is 0.58 eV. (b) The calculated formation energies per oxygen atom of the doubly positively charged oxygen chains for the electron chemical potential $\mu_e=0$ eV (a part of the data points for $N<11$ has been taken from Ref. 13).

inset of Fig. 1(a), where the calculated Kohn-Sham double-donor levels are shown. The R-type structure becomes more stable than the staggered one after $N=4$ [Fig. 1 (a)]. At the same time, the bistability disappears. In Ref. 16, the corresponding change takes place later, after $N=6$, leading, as mentioned earlier, to the TDD assignments differing from ours.

For $N>6$, where both the R-type and di-Y-lid chains are shallow donors, the R-type O chains have lower formation energies than the di-Y-lid-type ones (Fig. 1) except for $N=10$ where the formation energy of the di-Y-lid structure jumps anomalously below that of the R-type one. We have no explanation for this behavior, but believe that the jump at $N=10$ is due to the limited Γ -point sampling in the case of the elongated supercell. Furthermore, the $O_{4i}-O_{2Y}-O_{4i}$ chain has a high calculated activation energy for migration of about 2.5 eV, which is far too large to allow the formation of the higher TDDs in the consecutive sequence (see Chapter VI in Ref. 18). This makes the $O_{4i}-O_{2Y}-O_{4i}$ chain ($N=10$) a less favorable candidate for TDD8.

Figures 2(a)–2(d) show the calculated electron densities of the donor states for the $O_i-O_{nr}-O_i$ chains with $n=2,3$, and 11. The density is shown in the (110) oxygen plane in Figs. 2(a)–2(c). The side view is shown for $n=11$ in Fig. 2(d). It is immediately obvious that all the densities are dis-

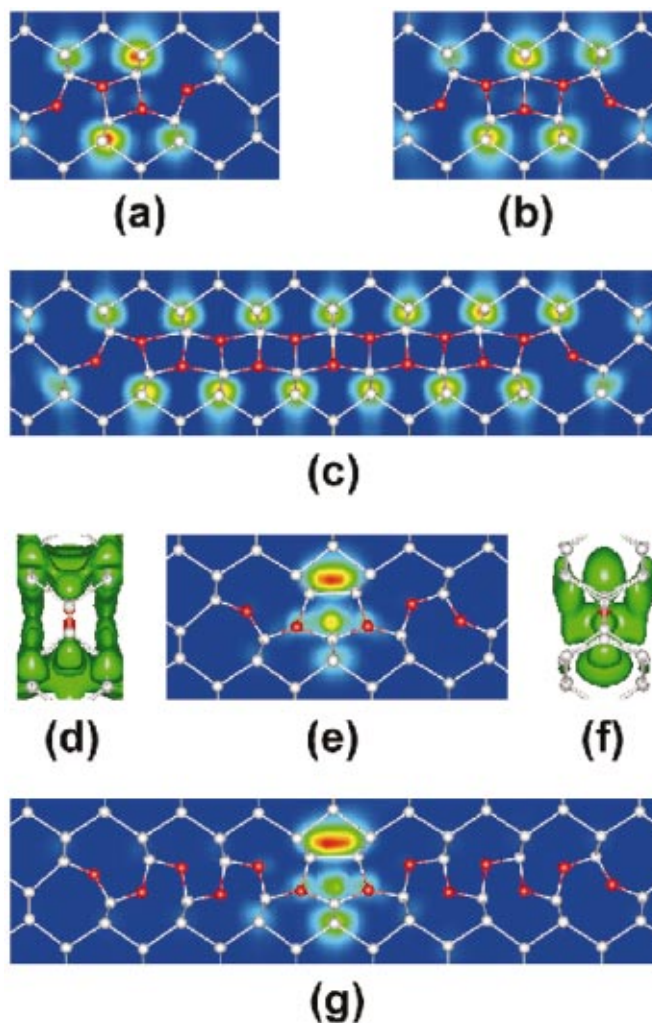


FIG. 2. (Color) Densities of the donor states. (a) $O_i-O_{2r}-O_i$ (TDD2) in the (110) plane, (b) $O_i-O_{3r}-O_i$ (TDD3) in the (110) plane, (c) $O_i-O_{11r}-O_i$ (TDD11) in the (110) plane, (d) Side view of the isosurface of the density of $O_i-O_{11r}-O_i$ (TDD11), (e) $O_i-O_{2Y}-O_{2i}$ in the (110) plane, (f) Side view of the isosurface of the density of $O_{5i}-O_{2Y}-O_{6i}$, and (g) $O_{5i}-O_{2Y}-O_{6i}$ in the (110) plane. In (d) and (f), the constant density surfaces drawn at 10% of the maximum value are shown. The red and gray balls denote the O and Si atoms, respectively. In (a)–(c), (e), and (g), the blue color represents minimum density and the red color maximum density.

tributed around the Si atoms *outside the region of O atoms* in agreement with the calculations of Ref. 16. This is consistent with the facts that the ^{17}O hyperfine splitting is hard to see in EPR experiments^{6,19} and that the analysis of the ^{17}O ENDOR lines reveals almost no hyperfine interaction, the line splitting being almost entirely due to quadrupole interaction.⁷

Figures 2(a)–2(c) show that the spin density of the donor state of the $O_i-O_{nr}-O_i^+$ chain has less extent along the C_2 symmetry axis than along the $[1\bar{1}0]$ chain direction, and becomes increasingly delocalized and anisotropic with increasing n , in agreement with ^{29}Si ENDOR experiments^{6,7} and the IR absorption experiment.¹⁰ Moreover, the O-chain structures in Figs. 2(b) and 2(c) contain a Si atom on the C_2 symmetry axis in agreement with ^{29}Si ENDOR experiments.^{6,7} However, the existence of a single O atom on the C_2 symmetry axis is in disagreement with the interpretation of ^{17}O ENDOR experiments.^{6,7} However, this ^{17}O ENDOR result may be somewhat uncertain because, as mentioned earlier, the ^{17}O hyperfine interaction almost vanishes.

The symmetry of the $O_i-O_{3r}-O_i$ ($N=5$) and $O_i-O_{11r}-O_i$ ($N=13$) chains is C_{2v} [Figs. 2(b) and 2(c), respectively], as it is also for the other $O_i-O_{nr}-O_i$ chains with odd n ($N=n+2$). The symmetry of the $O_i-O_{2r}-O_i$ chain ($N=4$) [Fig. 2(a)] is C_{1h} as it is also for the other $O_i-O_{nr}-O_i$ chains with even $n=4,6,8,\dots$ ($N=n+2$). However, the deviation of the symmetry of the core from C_{2v} decreases with increasing even n . The alternating behavior between C_{2v} and C_{1h} symmetries of the calculated $O_i-O_{nr}-O_i$ chain structures for odd and even n is consistent with the recent high-field EPR experiments that indicate that some TDD members have lower C_{1h} symmetry similarly to what has been found for the closely related NL10 family.^{5,8,9}

Figures 2(e)–2(g) show the calculated densities for the donor states of the $O_i-O_{2Y}-O_{2i}$ ($N=5$) and $O_{5i}-O_{2Y}-O_{6i}$ ($N=13$) chains. The spin density of the donor state of the $O_{5i}-O_{2Y}-O_{6i}^+$ chain is localized around O_{2Y} , and is very similar to and almost as localized as that of the $O_i-O_{2Y}-O_{2i}^+$ chain. The donor state densities of all the di-Y-lid structures have C_{2v} symmetry (or a symmetry very close to it). Although the calculated atomic structures of both the R-type and di-Y-lid-type O chains grow longer along the $[1\bar{1}0]$ chain axis with increasing n , the spin densities of *only* the R-type O chains become longer along the $[1\bar{1}0]$ chain axis [compare Figs. 2(a)–2(c) with 2(e) and 2(g)]. Thus the electronic and atomic structures of only the R-type O chains agree with the IR absorption¹⁰ and ²⁹Si ENDOR experiments.^{6,7} In addition, since the spin densities of the double-donor states of di-Y-lid-type O chains are significant at the O atoms [Figs. 2(e)–2(g)], there should be no difficulty in finding the ¹⁷O hyperfine splitting in EPR experiments, which is contrary to experimental findings.^{6,7,19}

In conclusion, we find that the R-type O chains provide a consistent model for the TDDs. This model transcends those based on the di-Y-lid-type O chains because R-type O chains (i) have lower formation energies; (ii) have both increasingly delocalized spin densities of the double-donor states and increasing structural anisotropy, in agreement with experiments; and (iii) have much lower activation energies for migration which leads, when these energies are used in a kinetic model, to a close agreement with the experimentally found consecutive kinetics of TDDs.^{14,18,20,21} Both the atomic structure and the spin density of the R-type $O_i-O_{nr}-O_i$ chains display alternating C_{2v} – C_{1h} symmetry, which is consistent with recent high-field EPR experiments. The spin densities of the double-donor states are located out-

side the region of the O atoms, consistent with the fact that the ¹⁷O ENDOR lines show almost no hyperfine interaction. Finally, we recall that the calculated local vibrational mode frequencies for the $O_{2i}-O_{2r}$ and $O_i-O_{nr}-O_i$ ($2 \leq n \leq 4$) chains agree closely with the experimental frequencies for TDD1–TDD4.^{17,22,23}

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